SCIENTIFIC CRITERIA DOCUMENT FOR THE DEVELOPMENT OF AN INTERIM PROVINCIAL WATER QUALITY OBJECTIVE FOR ANTIMONY

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AN INTERIM PROVINCIAL WATER QUALITY OBJECTIVE

FOR

ANTIMONY

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The public were notified of the proposed Interim Provincial Water Quality Objective for antimony through the Environmental Bill of Rights Electronic Registry and given the opportunity to comment in accordance with the Environmental Bill of Rights.

Preface

The Ontario Ministry of Environment and Energy develops Provincial Water Quality Objectives or Interim Objectives for those substances which are deemed to be of environmental concern in Ontario as determined through a screening process which considers persistence, potential to bioaccumulate, acute or chronic toxicity and potential presence in the aquatic environment. Alternatively, Ministry staff who have a direct responsibility for managing possible effects of these chemicals may request an evaluation.

Provincial Water Quality Objectives and Interim Objectives (PWQO/IOs) are numeric or narrative criteria intended to protect all life stages of aquatic organisms for indefinite exposures and/or to protect recreational uses of water. PWQO/IOs for recreational uses, including swimming, are currently based on microbiological and aesthetic considerations. The potential for harmful effects from exposure to chemical substances during recreational uses is unknown at present, but will be considered when scientific information becomes available. Ontario Drinking Water Objectives and sport fish consumption guidelines are also to be considered in protection of human health. PWQO/IOs represent a desirable water quality for the protection of designated uses of surface waters in Ontario. Objectives/Interim Objectives do not take into account analytical detection or quantification limits, treatability or removal potential, socio-economic factors, natural background concentrations, or potential transport of contaminants between air, water and soil. These factors are considered in policies and procedures which govern the uses of PWQO/IOs, contained in the booklet, Water Management (OMOEE 1994), which deals with all aspects of Ontario's water management policy.

The process for deriving these criteria is detailed in Ontario's Water Quality Objective Development Process (OMOE 1992a). The scientific and toxicology literature is reviewed for all of the following areas: aquatic toxicity, bioaccumulation, mutagenicity and aesthetic considerations. The final Objective/Interim Objective is based on the lowest effect concentration reported for any of these factors on aquatic organisms as well as taste and odour considerations of the water.

Where there are reliable and adequate data, a PWQO is derived by dividing the lowest adverse effect concentration by a safety factor. Where there are fewer data, an Interim Objective is developed using an "uncertainty factor". The size of the uncertainty factor reflects the quality and quantity of data available and the potential of the material to bioaccumulate.

PWQO/IOs are used to (i) identify surface waters of the Province which should not be further degraded. (ii) assess contaminant discharges to the aquatic environment and (iii) may be used as the basis for calculating water-quality based effluent limits specified in Certificates of Approval. Where better water quality is required to protect other beneficial uses of the environment in a given location, appropriate criteria and factors, including public health considerations, are taken into account.

Summary

An Interim Provincial Water Quality Objective (IPWQO) was developed for antimony for the protection of aquatic life. Available information on the physical-chemical properties, aquatic toxicity, bioaccumulation potential, taste and odour characteristics and genotoxicity potential of antimony were considered in developing the interim objective.

Antimony is an element which occurs naturally in the earth's crust. Most of the antimony in Canada is produced as a by-product of the refining of lead. Antimony is used in metal alloys to increase hardness and to decrease the melting point. Antimony is also used in a number of industrial and commercial uses. Recently, antimony has been approved for use as a pipe-solder replacement for lead.

Antimony is found in trace amounts in surface waters of Ontario. In the Great Lakes total antimony concentrations did not exceed 0.5 ug/L, however levels as high as 9100 ug/L (9.1 mg/L) have been reported in Canadian surface waters.

Antimony exists in surface waters mainly as the pentavalent and trivalent forms. Salts containing antimony are not very soluble in water. It is believed that bio-methylation of antimony salts may occur, however this process has not been clearly demonstrated. Removal of antimony from aquatic systems occurs through precipitation and sedimentation.

Compared to other metals, antimony is relatively non-toxic. The literature indicated that acute effects for a variety of aquatic life occurred between 1 mg/L and 1080 mg/L. Chronic effects ranged from 0.3 mg/L to 678 mg/L. Antimony does not appear to bioaccumulate to any significant degree in fish.

There was insufficient aquatic toxicity data available to derive a Provincial Water Quality Objective. Instead, an Interim Provincial Water Quality Objective (IPWQO) has been developed based on existing data. **The recommended IPWQO for antimony is 0.02 mg/L** derived by dividing the lowest observed effect concentration (7d-LC50) for the toad *Gastrophyne carolinensis* of 0.3 mg/L by an uncertainty factor of 14.5.

The proposed IPWQO is above the current Ontario Ministry of Environment and Energy routine laboratory detection limit of 5 ug/L. This value should be protective of effects due to aquatic toxicity and bioaccumulation. Data on whether antimony affects the taste and odour of water are unavailable. There are insufficient data to assess the mutagenic potential of antimony to aquatic organisms. Little mutagenic

data of any sort were found for this compound. It is suggested that further research be done on these effects.

Note: Concentrations in this document are expressed in a number of different units commonly used in scientific papers. the conversion factors are:

1 gram per litre (g/L)	= 1000 milligrams per litre (mg/L)
1 mg/L	= 1000 micrograms per litre (ug/L)

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1.0 INTRODUCTION

Antimony (Sb) is a group V metalloid element which is present in a number of metallic and non-metallic forms (Emsley 1991). The metallic form is bright, silvery, hard and brittle (Emsley 1991). It has a melting point of 630° C, a boiling point at 1635° C (Windholtz *et al.* 1976) or 1380° C (Weiss 1980) and a density of 6.691 g/mL at 20° C (Weast 1979). It reacts with sulphur and chloride to form pentavalent sulphides and chlorides, and its principal oxidation states are +3 and +5. Concentrations of antimony in the earth's crust range from 0.2 to 1.0 ppm (Seiler 1988; Oehme 1979).

Antimony occurs in nature as the mineral stibnite and as antimony ores such as valentinite, livingstonite, cervantite and jamisonite which are mined in China, Mexico, and Bolivia (Windholtz *et al.* 1983). Antimony is not mined or refined in Ontario. Antimony is enriched in mineral tailings in Ontario (256 ppm average, 10 to 1590 ppm range, n ≈100) and could present environmental problems under specific conditions. In Ontario, antimony occurs in combination with sulphur. Sulphur-metal combinations, from an environmental standpoint, are considered to be unstable (OMOE 1979). However, there have been no reports of antimony causing major environmental problems in Ontario.

1.1 PRODUCTION AND USES

The use of antimony has a long history. Stibnite (black sulphide) was used in biblical times as a cosmetic to darken women's eyebrows. Antimony has been found as worked metal artifacts as far back as 4000 BC, and has been mentioned in writings from ancient Egypt and Greece (Greenwood and Earnshaw 1984).

Presently, most of the antimony in Canada is produced as a by-product of the refining of lead in British Columbia and New Brunswick (CCREM 1987). Jacques and Kosteltz (1988, as cited in Government of Canada 1991) reported that Canadian antimony emissions to all media was 75 tonnes, with 75% of total emissions attributed to lead and zinc production. Giancola (1994) reported that Canadian production of antimony in 1993 was 622 000 kg, worth approximately $1.358 million. This was down from 796 000 kg in 1992. Most of the antimony was produced in British Columbia and New Brunswick. Manitoba produced 3000 kg in 1993 and Ontario did not produce antimony in 1992 or 1993. NRC (1993) reported that approximately 400 000 kg of antimony were consumed in 1991. This was approximately 95% of the total antimony produced. In 1992, consumption was down to approximately 360 000 kg, while production was up, resulting in only 46% of the antimony being produced in Canada being consumed locally. NRC (1993) reported that the average price of antimony has risen from 1991 to 1993, and was $2.187 per kilogram in 1993.

Due to the brittleness of antimony, it is commonly used in alloys of lead, bismuth, tin, copper, nickel, iron, and cobalt, in order to increase hardness and to decrease the melting point (USEPA 1980). Antimony is also used in ammunition, bearings, storage battery grids, pewter, rubber, matches, ceramics, enamels, lacquers, paints, and textiles (USEPA 1980; Oehme 1979). One of the most commercially important antimonial compounds is antimony trioxide, which is used as a flame retardant (LeBlanc and Dean 1984; USEPA 1980). Biological uses of antimony (especially antimony potassium tartrate) as an emetic, expectorant, parasiticide, insecticide, and/or a purging agent have decreased over time (Jernejcic 1969; Tamulinas 1979; Oehme 1979). There are currently no antimony-containing pesticides registered for use in Ontario (Radzius pers. comm.). Recently antimony has been approved for use as a pipe solder to replace lead.

1.2 AQUATIC SOURCE AND FATE

The current OMOEE laboratory detection limit for antimony in water is 5 ug/L, however this may vary from 0.05 ug/L to 50 ug/L depending on the contamination of the sample (Boomer, Laboratory Services Branch, OMOEE, Pers. Comm.). The current atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emissions (ICP-AES) analyzation detection limits in water are 3 ug/L and 32 ug/l, respectively (US DHHS 1992).

Antimony enters the aquatic environment via runoff from the natural weathering of rocks, and as soil leachate. Antimony can be released from natural discharges including wind-blown dust, volcanic eruption, sea spray and forest fires (USDHHS 1992). Effluents from mining and manufacturing operations, as well as discharges from industries and sewage treatment plants are the major sources of aquatic contamination of antimony. Anthropogenic sources of antimony also include industrial dust, automobile exhaust and combustion products of fossil fuels (Seiler 1988). Coal and petroleum contain from 0.5 to 5 ppm and 30 to 107 ppm antimony, respectively (Brown 1983; Jungers *et al.* 1975). Although concentration of antimony in Ontario discharges are generally low (below 1 ug/L), concentrations as high as 7 mg/L were measured in mine wastewaters in New Brunswick (Doe *et al.* 1987). Antimony is used in chemical fertilizers with concentrations as high as 100 mg/kg, thus fertilizers can be an important antimony source in agricultural communities (Coughtrey *et al.* 1983).

Antimony may also enter aquatic systems as a component of dry and wet atmospheric deposition. Coal-fired power plants, copper smelters and inorganic chemical plants release antimony into the atmosphere. Urban air averages about 0.001 $\mu g/m^3$ with a maximum of 0.160 $\mu g/m^3$ (USEPA 1980; Oehme 1979). Little

data was available which recorded levels of antimony in air in Ontario. A study of the effects on air quality of a hospital incinerator in London, Ontario recorded levels as high as 0.177 ug/m^3 in the area, however long term averages (1989 to 1993) were less than the detection limit of 0.001 ug/m^3 (OMOEE unpublished data).

Recent effluent discharge data are available from Ontario's Municipal/Industrial Strategy for Abatement (MISA) monitoring reports. Ten sectors (iron and steel, organic chemical manufacturing, pulp and paper, metal mining, metal casting, industrial minerals, inorganic chemicals, petroleum, waste water treatment plants and hydro-electric generation) were required to monitor effluent quality for a one year period (OMOE 1988, 1990, 1991a-f, 1992b, 1993). Quantification of the total mass (effluent flow rate X effluent concentration) of antimony discharged to Ontario's surface waters could not be determined reliably since many of the antimony concentrations in the effluents were at or below the regulatory method detection limit (RMDL). The RMDL represents the lowest level generally measurable using modern analytical procedures (OMOE 1992b). In the case of antimony, the RMDL was 5 ug/L. The data do indicate however that antimony discharges seem to be greatest in the mining and iron and steel sectors. According to MISA monitoring data, the mining sector discharges about 1770 kg/year, of which 98% is attributable to the gold mining sub-sector (OMOE 1991a).

Antimony is found in trace amounts in surface waters of Ontario, mainly as a result of natural inputs (OMOE 1981). The reported antimony concentrations in surface waters of Canada range from 0.001 to 9.1 mg/L (CCREM 1987). The USEPA (1980) reported an average ambient surface water concentration in freshwater streams of 1.1 µg/L. Rossmann and Barres (1988) measured the dissolved, particulate and total concentrations of antimony in water samples from the Great Lakes. These values are summarized in Table 1. Samples were analyzed using

flameless atomic absorption spectrophotometry. "Dissolved" refers to the amount of antimony passing through a 0.5 μm pore size filter. This may include antimony associated with very small particles and colloids. "Particulate" refers to the antimony associated with particulate matter retained on a 0.5 μm pore size filter that was extracted with a hot solution of nitric acid and hydrogen peroxide. The authors reported that in many cases, concentrations on particulate matter were not detectable. "Total" antimony refers to results derived from the direct injection of unfiltered samples into the graphite furnace.

Table 1: Median concentrations of antimony in water samples from the Great Lakes (from Rossmann & Barres, 1988). Values in μg/L.

Lake (Sample Date)	Dissolved	Particulate	Total
Huron (1981)	0.5	-	0.22
Erie (1981)	0.17	-	0.085
Michigan (1981)	0.23	0.003	0.25
Superior (1983)	0.082	-	0.072
Ontario (1985)	0.16	-	0.17

- = not detectable or no analysis

1.3 AQUATIC CHEMISTRY

In surface waters, antimony exists predominantly in either the pentavalent or trivalent form. Callahan *et al.* (1979) reported that the trivalent form occurs under moderately oxidizing conditions while the pentavalent form predominates in highly oxidizing environments. In reducing environments, stibine gas (SbH_3) may be formed; however, stibine is not stable in aerobic waters and is hydrolyzed to form oxides. Antimony (III) does not occur as a free ion (Sb^{3+}) in water. Rather, it will occur as the cation antimony oxide (SbO^+) or as antimony oxychloride (SbOCl) with SbO^+

predominating (Burns *et al.* 1981). Antimony oxychloride further transforms to antimony trioxide (Sb_2O_3) which precipitates out. Brooke *et al.* (1986) reported that high chloride concentrations result in a decrease in the precipitation of antimony, presumably by inhibiting the rate of this process. Antimony salts are of sufficient solubility to keep antimony in solution, except in cases of heavy antimony loadings. The degree of solubility of the salts varies considerably. For example, antimony trioxide is only slightly soluble in water, whereas antimony trichloride is much more soluble.

While the exact rates are not known, sorption processes are normally the most important mechanisms for removal of antimony from solution. Precipitation as antimony trioxide or antimony oxychloride may also limit soluble antimony concentrations in waters (USEPA 1988). Antimony has an affinity for clay and minerals but the effect of sorption on the fate of antimony in aquatic systems remains unknown.

Co-precipitation with hydrous iron, manganese and aluminum may also occur (USEPA 1979). Since sediments may offer a reducing environment, the formation of stibine can result in the remobilization of antimony, which had previously been adsorbed to sediments.

Alkylated forms of antimony have been found in natural waters (Bodek *et al.* 1988). Biomethylation may be an important process in the mobilization of antimony from reducing sediments (Andreae *et al.* 1981). Bodek *et al.* (1988) reported that while biomethylation in the natural environment has not been clearly demonstrated, it probably occurs because of its chemical similarity to tin, lead, arsenic, and selenium.

All of these elements have been shown to be biomethylated in the aquatic environment.

2.0 TOXICITY TO AQUATIC ORGANISMS

Toxicity of antimony to aquatic organisms seems to be directly proportional to its aqueous solubility (Tamulinas 1979). The order of increasing toxicity and solubility is pentoxides and trioxides, pentasulphides and trisulphides, antimony metal, and antimony potassium tartrate. USEPA (1988) reported that soluble concentrations of antimony can be obtained using antimony trichloride, however this results in a transformation of antimony to antimony oxychloride and subsequently to antimony trioxide.

All candidate toxicological information is screened for acceptability. All information that meets the following requirements is considered primary data:

- Toxicity tests must employ accepted laboratory practices of exposure and environmental controls. While all tests must be evaluated on a case by case basis, those tests following published protocols of government agencies or standard setting associations are generally acceptable.

- Any tests may be acceptable, including static tests if it can be shown that concentrations of the toxicant are not changing (significantly) throughout the test and adequate environmental conditions for the test species are maintained with respect to such factors as dissolved oxygen and removal of metabolic wastes. Generally, continuous flow exposures, and renewal tests (i.e. static tests with replacement) are acceptable if appropriate rates of renewal of toxicant are maintained. Static tests are acceptable if concentrations of the

toxicant are measured in the exposure vessel at the beginning and end of the test and no more than 10% of the toxicant is lost during the test. The use of chemical carriers is acceptable as long as the concentration of the toxicant does not exceed water solubility in the absence of the carrier. Appropriate chemical carrier controls must also be included.

- Dissolved concentrations of toxicant in the exposure vessels must be constant and verified by measurements rather than calculated or measured only in stock solutions. Tests will generally be considered unacceptable if more than 10% of the toxicant is lost during the test.

- Test end points and lengths of exposure must be appropriate to the life stage of the species tested and the characteristics of the substance. Although the definitive bench mark for chronic toxicity is a whole life cycle test, partial life cycle and short term or early life stage tests are acceptable as chronic data.

- Relevant environmental parameters such as temperature, pH and hardness must have been recorded.

- Responses and survival of controls must be appropriate for the species and test used.

Data on vertebrates and invertebrates not meeting all of the above are denoted as secondary in objective development documents. Secondary data are inadmissible in the derivation of an Objective but are admissible in deriving an Interim Objective. Most tests using aquatic plants will also be classified as secondary due to the frequent use of artificial media or a lack of standardized protocols; however, plant data may be used as the critical endpoint for Objective development subject to best scientific judgement.

Toxicity information in this document is current as of February 1995.

2.1 ACUTE TOXICITY

2.1.1 Vertebrates

There were two primary, acute values available for vertebrates. Doe *et al.* (1987) reported a 96h-LC50 for rainbow trout (*Oncorhynchus mykiss*) fingerlings of 37 mg/L as antimony tartrate, while Kimball (unpublished MS) reported a 96h-LC50 for 8 week old fathead minnows (*Pimephales promelas*) of 21.9 mg/l as antimony trichloride.

In addition, there were twelve secondary acute toxicity values, with three species of fish. All but one study reported 96h-LC50s, the remaining test reported 45% mortality at 96 h. Toxic endpoint concentrations of antimony ranged from 9 to >530 mg/L (See Table 2, Figure 1). There appeared to be no difference in sensitivity among species tested.

Tarzwell and Henderson (1960) reported the toxicity of three antimony compounds in soft and hard water using fathead minnows. The trichloride was slightly more toxic than potassium tartrate. The trioxide was the least toxic, probably due to its low solubility. There was no consistent effect of hardness on antimony toxicity.

Buccafusco *et al.* (1981) reported that the 96h-LC50 of antimony trioxide for Bluegill (*Lepomis macrochirus*), to be >530 mg/L under static conditions. The concentration of antimony was not measured during the test and there was excess compound in the water.

2.1.2 Invertebrates

There were six primary acute toxicity data points for invertebrates, all 48h-LC50s with *Daphnia magna*. Effect concentrations ranged from 2.7 to 18.8 mg/L (Doe *et al.* 1987, Kimball unpublished MS).

Secondary acute toxicity data were available for three species of invertebrates. Toxic concentrations of antimony ranged from 3.5 mg/L based on a 48h-LC50 to *Ceriodaphnia dubia* (USEPA 1988) to 1080 mg/L for the tubificid, *Tubifex tubifex* (Khangarot 1991).

While most data suggests that daphnids are more sensitive than other invertebrates, data from Khangarot and Ray (1989) suggest otherwise. These authors reported a 48h-EC50 of 423.5 mg/L for *Daphnia magna*, which was almost 100 times higher than most of the acute values for antimony in the literature. Only data from LeBlanc (1980 ; 48h no effect concentration (NOEC) >530 mg/) supports their data. The large difference in antimony toxicity to *Daphnia magna* may be due to the compounds tested. It does not appear that water quality characteristics, such as temperature, pH or hardness are the reason.

Khangarot and Ray (1989) reported that the low toxicity of antimony trioxide was due to the salt's limited solubility in test water, yet they did not report the existence of a precipitate during the experiment, which they had observed in tests with other metals. Because the data from Khangarot and Ray (1989) and LeBlanc (1980) are both secondary data (i.e. antimony concentrations were not measured) there is the possibility that antimony concentrations decreased so drastically in the test solutions that it appeared that large doses of the chemical were required to cause a toxic response.

2.2 CHRONIC TOXICITY

2.2.1 Vertebrates

There were five primary chronic toxicity values for vertebrates (Table 2). Values ranged from 0.3 mg/L antimony trichloride for a 7d-LC50 with larval toads (Birge 1978) to 16 mg/L antimony tartrate for a 30d-LC40 with rainbow trout fingerlings (Doe *et al.* 1987). Chronic toxicity of antimony trichloride to fathead minnows was determined by Kimball (unpublished MS) starting with eggs <40-h old and lasting until 28 days post hatch. At 28 d, survival was significantly decreased to 70% at 9.31 mg/L and 53% of controls at 19.11 mg/L, but growth was the most reduced. Fish exposed to 2.31 mg/L were significantly shorter than the controls (24.7 mm compared to 25.9 mm).

LeBlanc and Dean (1984) exposed embryo-larval stages of fathead minnows to antimony trioxide for 30 d. The exposure concentrations ranged from 0.00062 to 0.0075 mg/L. The solution was saturated at 0.0075 mg/L and at this concentration there was no effect on survival, hatching, and growth.

Tamulinas (1979) exposed ten channel catfish (*Ictalurus punctatus*) to 100 mg/L suspension of antimony trioxide for 30 d. The suspension of antimony trioxide settled to the bottom of the aquaria in 3-4 d and the measured concentration of antimony in the water was 1.2 mg/L. Three channel catfish were then exposed to 4 mg/L of the more soluble antimony potassium tartrate. Concentrations were not measured during the test. Toxicity endpoints measured in both experiments were the health of gill arches (erosion or hyperplasia), red blood packed cell volume (PCV), and concentrations of serum glutamic oxaloacetic transaminase (SGOT), and glutamic pyruvic transaminase (SGPT). None of these endpoints were significantly affected by either form of antimony.

2.2.2 Invertebrates

There were four primary chronic toxicity data points found in the literature. A 30-d LC50 of 2.7 mg/L was estimated for *Daphnia magna* exposed to antimony potassium tartrate (Doe *et al.* 1987). The chronic toxicity of antimony chloride to *Daphnia magna* was determined by Kimball (unpublished MS). He reported a 28-d LC50 of 4.51 mg/L, but the number of young produced declined significantly at 0.88 mg/L. However, the dose-response relation was very weak, which suggests that survival was a clearer endpoint than reproductive effects in this experiment.

Doe *et al.* (1987) reported *D. magna* chronic NOECs based on reproductive impairment and growth of 1.7 and 0.8 mg/L, respectively.

Secondary chronic toxicity information was available for 6 species of invertebrates. Values ranged from 0.5 mg/L for a 96h-EC50 with *Hydra* (Brooke *et al.* 1986) to 680 mg/L for a 96h-EC50 with *Tubifex tubifex* (Khangarot 1991).

2.2.3 Other organisms (Bacteria, Protozoa, Algae, Macrophytes)

Den Dooren De Jong (1965) evaluated the tolerance of *Chlorella vulgaris* to metallic anions. A chronic exposure of 3 to 4 months in growth media containing antimony oxychloride resulted in NOEC and LOEC values of 0.032 and 0.064 mmol/L (3.9 and 7.8 mg/L), respectively. The endpoint criterion was inhibition of growth. Concentrations of the test solutions were not measured. The 96h EC50 values for *Selenastrum capricornutum* exposed to antimony trioxide were 0.61 and 0.63 mg/L resulting in a decrease in chlorophyll *a* content, and a reduction in cell numbers, respectively (USEPA 1978). Brooke *et al.* (1986) reported that duckweed (*Lemna minor*) exposed to 25.5 mg/L over 96h showed reduced growth.

2.3 SUMMARY OF TOXICITY DATA

Insufficient data prohibits comparison of the relative toxicities of the various forms of antimony to aquatic biota.

In general, toxic concentrations from primary references indicated effects around the 1 to 20 mg/L range, while secondary values reached as high as 1000 mg/L. Vertebrates and invertebrates appeared to be equally sensitive to acute exposure to antimony. Plants, vertebrates and invertebrates appeared to be equally sensitive to antimony under chronic exposures.

Compared to other metals, antimony is relatively non-toxic. Khangarot and Ray (1989) determined the toxicity of 23 metals using daphnids. They reported that antimony was among the least toxic of metal ions to daphnids, with only potassium, calcium, magnesium and sodium being less toxic. The authors also reported that their unpublished data using an ostracod, *Cyprio subglubosa*, also showed antimony to be among the least toxic of 28 metals, with only barium, potassium, calcium, sodium and magnesium being less toxic during 48h exposure tests. Furthermore, a later study by Khangarot (1991) examined the toxicity of 32 metals to *Tubifex tubifex* and ranked antimony the second lowest of 32 metals based on 48h and 96h toxicity tests. Only sodium was less toxic than antimony to *Tubifex*. Doe *et al.* (1987) found that the hardness of test solutions did not affect the toxicity of antimony, based on five hardness levels (see Table 2). Kimball (unpublished MS) tested neonate (<24h old) daphnids for 48h or 96h, with or without feeding. The author reported that feeding had no effect on the toxicity of antimony.

3.0 BIOACCUMULATION

There is a paucity of information concerning the bioaccumulation of antimony by aquatic organisms. Maximum bioconcentration factors (BCFs) of 40 and 16,000

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3.0 BIOACCUMULATION

There is a paucity of information concerning the bioaccumulation of antimony by aquatic organisms. Maximum bioconcentration factors (BCFs) of 40 and 16,000

have been reported for freshwater fish and invertebrates, respectively (Chapman *et al.* 1968). However, whole body analysis of bluegill and rainbow trout demonstrated that antimony does not bioaccumulate to any great extent (i.e. greater than 1000 times the water concentration) in freshwater vertebrates (Doe *et al.* 1987; USEPA 1980; Barrows *et al.* 1980). Doe *et al.* (1987) reported a BCF of 3.4 in rainbow trout.

The influence of organism size on metal concentration in aquatic insects was examined by Smock (1983). The concentration of antimony decreased exponentially with increasing body size (whole-body dry weight) suggesting that surface adsorption was important in the bioaccumulation of antimony. However, because antimony exists as a negatively-charged oxyanion, it is unlikely to be readily adsorbed. Further investigation showed that the gut contained antimony-enriched particles. Smock (1983) concluded that both adsorption and absorption influence the bioaccumulation of antimony in aquatic insects. In any event, actual uptake into the body of insects is low.

Bioaccumulation of antimony in lake trout (*Salvelinus namaycush*) was not affected by age. Tong *et al.* (1974) collected native lake trout ranging in age from 1 to 12 years. Antimony concentrations in whole fish weight ranged from 0.46 to 0.86 µg/kg and did not vary significantly with age, indicating that antimony does not bioconcentrate in fish.

Barrows *et al.* (1980) measured antimony residues in fish that were continuously exposed to antimony trioxide for 28 d, followed by a 7-d depuration period. Whole body residues in exposed fish (mean body lengths ranging from 25 to 35 mm) were no greater than those in the controls.

Channel catfish were exposed to measured concentrations of 1.2 mg/L of antimony trioxide or 3 to 5 mg/L antimony potassium tartrate. After 30 days, the tissue concentrations ranged from 0.26 to 6.87 mg/kg and 0.83 to 8.35 mg/kg for the two

chemicals, respectively. The average tissue concentration in control animals was 0.158 mg/kg (Tamulinas 1979). The calculated BCF value for antimony trioxide was 1.81, based on an average tissue concentration of 2.169 mg/kg and water concentration of 1.2 mg/L. The BCF for antimony potassium tartrate was 0.44, based on an average tissue concentration of 1.76 mg/kg and a water concentration of 4 mg/L (Tamulinas 1979).

Wood and Wang (1985) reported that antimony is one of several elements known to form methyl-metal compounds in environmental exposures, and therefore may bioaccumulate. Levels of bioaccumulation, however were not given.

4.0 ODOUR AND TASTE

No data were found concerning the odour or taste effects of antimony or antimony compounds on the quality of water or aquatic biota destined for human consumption.

5.0 MUTAGENICITY

No mutagenicity data using aquatic organisms were found in the literature. The IRIS (1994) reported that the USEPA has not evaluated antimony for evidence of human carcinogenic potential. Sharma and Talukder (1987) reported that clastogenic information on antimony was not available. One report (Sitig 1981) states that antimony trioxide may be a carcinogen. Due to the paucity of data, at this time it is not possible to assess the mutagenic properties of antimony.

6.0 DERIVATION OF INTERIM OBJECTIVE

The minimum data base to develop a Provincial Water Quality Objective was not met for this chemical. An additional primary chronic invertebrate study is required. As well, a more complete study of the potential that antimony may have to cause mutagenic effects on aquatic organisms is needed. Therefore an Interim Provincial Water Quality Objective was developed by completing the Uncertainty Factor Worksheet (Table 3). The requirements to develop a PWQO/IO are described in more detail in OMOE (1992a).

6.1 CALCULATION OF FINAL UNCERTAINTY FACTOR

The Uncertainty Factor Worksheet (Table 3) uses both acute and chronic toxicity data. Up to three different species of fish, and two species of invertebrates from different orders may be used. One test with an algae or an aquatic plant species is also permitted. Algal exposures are considered chronic according to the OMOE (1992a) protocol due to their shorter life span. A baseline uncertainty factor is selected - either 1000 or 10000 based on whether the substance is, or has the potential to be, bioaccumulative.

The baseline uncertainty factor for inorganics is 1,000 unless there is evidence of significant bioaccumulation in aquatic biota (OMOE 1992a). While one study reports a BCF in invertebrates of 16 000, most data suggests that antimony does not significantly bioaccumulate in fish (see section 3.0). Thus, the baseline uncertainty factor for antimony is 1,000.

The final uncertainty factor was calculated based on the following toxicity information:

The following data were used in the acute category:

- The 96h-LC50 of 21.9 mg/L for fathead minnows was considered as primary information (Kimball, undated manuscript)

- The 96h-LC50 of 37 mg/L for rainbow trout was considered primary information (Doe *et al.* 1987)

- The 7d-LC50 of 11.3 mg/L for goldfish was considered primary information and was used in lieu of an additional primary acute study (Birge 1978)

- The 48h-LC50 of 5 mg/L for *Daphnia magna* was considered primary information (Doe *et al.* 1987)

- The 96h-LC25 of 25.7 mg/L was considered secondary information because there was a greater than 10% loss of toxicant during the experiment (Brooke *et al.* 1986)

The following data were used in the chronic category:

- The 30d-LC50 of 16 mg/L for rainbow trout was considered primary information (Doe *et al.* 1987)

- The 30d-LOEC (growth) of 2.3 mg/L for fathead minnows was considered primary information (Kimball, undated MS)

- The 7d-LC50 of 0.3 mg/L for toads was considered primary information (Birge 1978)

- The 96h-EC50 (immobility) for of 0.5 mg/L for *Hydra sp.* was considered secondary information because toxicant concentrations varied by more than 10% during the experiment (Brooke *et al.* 1986)

- The 30d decrease in reproduction in *Daphnia magna* caused by 1.7 mg/L antimony was considered primary data (Doe *et al.* 1987).

- The 96h reduction in growth in the duckweed, *Lemna minor*, caused by 25.5 mg/L antimony was considered secondary data (Brooke *et al.* 1986)

Using the above information and applying the appropriate calibration factors, a value of 14.5 was calculated as the final uncertainty factor (Table 3).

6.2 CALCULATION OF THE INTERIM OBJECTIVE VALUE

The Interim Objective is set as a single value independent of other water quality parameters such as temperature or water hardness. The lowest measured adverse effect value was the chronic toxicity value of 0.3 (Birge 1978) for embryo/larvae of the toad, *Gastrophryne carolinensis*. This value divided by the final uncertainty factor of 14.5 produced an Interim PWQO of 0.02 mg/L. This value is above the ambient concentration of antimony in surface waters as reported by USEPA (1980), but is much lower than the MATC of 1.2 mg/L recommended by Doe *et al.* (1987).

The Interim Provincial Water Quality Objective for antimony that is recommended for the province of Ontario is 0.02 mg/L.

7.0 RESEARCH NEEDS

Currently, there is insufficient toxicity data to support the derivation of a PWQO. One chronic study using an invertebrate other than a crustacean is needed to complete the toxicity requirements to develop a PWQO.

Mutagenicity studies with aquatic organisms should be performed to assess whether the proposed PWQO will protect aquatic organisms from these effects.

There is a need to evaluate the toxicity of antimony and antimony compounds with varying water quality characteristics such as hardness and pH.

8.0 OBJECTIVES FROM OTHER AGENCIES

CCREM (1987) did not recommend a guideline/criteria for antimony because of insufficient toxicity information.

USEPA (1988) has produced draft guidelines of 0.03 mg/L as a 4d average concentration, not to be exceeded more than once every 3 years on average and 0.088 mg/L as a 1-h average concentration not to be exceeded more than once every 3 years on average.

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Appendices

Table 2. Aquatic Toxicity Table for Antimony

Common Name	Species Name	Life Stage	(1) Response	pH	Temp. (°C)	DO (mg/L)	Alk. (mg/L)	Hard. (mg/L)	Effect Conc. (mg/L)	(2) Chem Spec.	(3) Data Code	Reference	(4) Data Class
VERTEBRATES													
Rainbow trout	*Oncorhynchus mykiss*	fingerling (1.2 g)	96h-LC50	6.7-7.3	15	-	-	25	37	A	SM	Doe et al. 1987	PA
		fingerling (23 mm)	96h 45% dead	7.1	15	71%	37	52	>25.7	C	SM	Brooke et al. 1986	SA
		embryo/larval	28d-LC50	7.4	13	sat	-	104	0.58	C	RM	Birge 1978	SC
		fingerling	30d-LC50	6.7-7.3	15	-	-	25	16	A	RM	Doe et al. 1987	PC
Goldfish	*Carassius auratus*	embryo/larval	7d-LC50	7.4	22	sat	-	195	11.3	C	RM	Birge 1978	PC
Toad	*Gastrophryne carolinensis*	embryo/larval	7d-LC50	7.4	22	sat	-	195	0.3	C	RM	Birge 1978	PC
Fathead minnow	*Pimephales promelas*	30d old (19 mm)	24h-EC50	7.1	21	76%	38	48	20.8	B	SM	Brooke et al. 1986	SA
		30d old (19 mm)	24h-LC50	7.1	21	76%	38	48	20.8	B	SM	Brooke et al. 1986	SA
		30d old (19 mm)	48h-EC50	7.1	21	76%	38	48	17.4	B	SM	Brooke et al. 1986	SA
		30d old (19 mm)	48h-LC50	7.1	21	76%	38	48	17.4	B	SM	Brooke et al. 1986	SA
		30d old (19 mm)	96h-EC50	7.1	21	76%	38	48	14.4	B	SM	Brooke et al. 1986	SA
		embryo/larval	96h-LC50	8.2	-	-	360	400	12	A	??	Tarzwell and Henderson 1960	SA
		8 weeks old	96h-LC50	8.0	25	6.9	232	-	21.9	C	FM	Kimball (unpublished MS)	PA
		embryo/larval	96h-LC50	7.4	-	-	18	20	9	C	??	Tarzwell and Henderson 1960	SA
		embryo/larval	96h-LC50	7.4	-	-	18	20	20	A	NP	Tarzwell and Henderson 1960	SA
		embryo/larval	96h-LC50	7.4	-	-	18	20	>80	B	??	Tarzwell and Henderson 1960	SA
		embryo/larval	96h-LC50	8.2	-	-	360	400	17	C	??	Tarzwell and Henderson 1960	SA
		embryo/larval	96h-LC50	8.2	-	-	360	400	>80	B	??	Tarzwell and Henderson 1960	SA
		adult	96h-LC50	7.2-7.9	-	-	30-35	0-48	833		SM	Curtis and Ward 1981	SA
		30d old (19 mm)	96h-LC50	7.1	21	76%	38	48	14.4	B	SM	Brooke et al. 1986	SA
		8 weeks old	30d-LOEC (growth)	8.0	25	6.9	234	-	2.3	C	FM	Kimball (unpublished MS)	PC
		8 weeks old	30d-LOEC (lethality)	8.0	25	6.9	234	-	9.3	C	FM	Kimball (unpublished MS)	PC
		embryo/larval	30d-NOEC (surv., hatch, growth)	6.2-7.3	25	8.7	-	34	0.0075	B	FM	LeBlanc and Dean 1984	SC
Channel catfish	*Ictalurus punctatus*	fingerling (8 inch)	30d-NOEC (PCB, SGOT, SGPT)	-	-	-	-	-	1.2	B*	SM	Tamulinas 1979	SC
		fingerling (8 inch)	30d-NOEC (PCB, SGOT, SGPT)	-	-	-	-	-	4	A	SU	Tamulinas 1979	SC
		fingerling (3-5 inch)	spleen wt./body wt.	-	-	-	-	-	3-5	B	RM	Tamulinas 1979	SC
Bluegill	*Lepomis macrochirus*	0.32-1.2g	96h-LC50	6.7-7.5	21-23	7-8.8	28-34	2-48	>530	B	SU	Buccafusco et al. 1981	SA
		0.5g	96h-LC50	6.8-7.4	23	5.6-6	-	4-46	>25.8	C	SM	USEPA memo 1988	SA

Table 2. Aquatic Toxicity Table for Antimony

Common Name	Species Name	Life Stage	(1) Response	pH	Temp. (°C)	DO (mg/L)	Alk. (mg/L)	Hard. (mg/L)	Effect Conc. (mg/L)	(2) Chem Spec.	(3) Data Code	Reference	(4) Data Class
INVERTEBRATES													
water flea	*Daphnia magna*		24h-EC50 (immob.)	7.6	13	5.6	400	240	555.3	B	SU	Khangarot and Ray 1989	SA
			48h-EC50 (immob.)	7.6	13	5.6	400	240	423.5	B	SU	Khangarot and Ray 1989	SA
		<24h old	48h-LC50	–	–	–	–	–	9		SU	Bringmann and Kuhn 1979	SA
		<24h old	48h-LC50	7.8	20	–	–	92	5	A	SM	Doe et al. 1987	PA
		<24h old	48h-LC50	7.8	20	–	–	220	2.7	A	SM	Doe et al. 1987	PA
		<24h old	48h-LC50	7.8	20	–	–	250	6.7	A	SM	Doe et al. 1987	PA
		<24h old	48h-LC50	7.8	20	–	–	31	5	A	SM	Doe et al. 1987	PA
		<24h old	48h-LC50	7.8	20	–	–	45	5	A	SM	Doe et al. 1987	PA
		<24h old	48h-LC50 (unfed)	8.2	20	7.9	–	–	18.8		SM	Kimball (unpublished MS)	PA
		<24h old	48h-NOEC	8	22	>60%	–	173	>530		SU	LeBlanc 1980	SA
		lifecycle	64h-LC50	–	–	–	–	–	19.8		SM	Anderson 1948	SA
		<24h old	96h-LC50	8.2	20	7.9	–	–	12.1		SM	Kimball (unpublished MS)	PC
		lifecycle	28d-LC50	8.5	20	7.4	–	225	4.5		RM	Kimball (unpublished MS)	PC
		<24h old	30d-LC50	7.8	20	–	–	250	1.7	A	RM	Doe et al. 1987	PC
		<24h old	30d-NOEC (reproduction)	7.8	20	–	–	250	0.8	A	RM	Doe et al. 1987	PC
water flea	*Ceriodaphnia dubia*	<24h old	48h-LC50	8	25	8.2	Lake Superior		3.5		SM	EPA memo 1987	SA
	Hydra sp.	adult	24h-EC50	7.7	24	90%	41	47	2.0	C	SM	Brooke et al. 1986	SA
	Hydra sp.	adult	48h-EC50	7.7	24	90%	41	47	1.0	C	SM	Brooke et al. 1986	SA
	Hydra sp.	adult	96h-EC50	7.7	24	90%	41	47	0.5	C	SM	Brooke et al. 1986	SC
annelid	*Lumbriculus variegatus*	23mm/6mg	96h-NOEC	7.1	16	71%	37	52	25.7	C	SM	Brooke et al. 1986	SC
amphipod	*Gammarus pseudolimnaeus*	14 mg/7mm	96h-LC50	7.1	16	71%	37	52	25.7	C	SM	Brooke et al. 1986	SC
caddisfly	*Pycnopsyche sp.*	18mm/113 mg	96h-NOEC	7.1	16	71%	37	52	25.7	C	SM	Brooke et al. 1986	SC
nematode	*Caenorhabditis elegans*	adults (3-4d old)	96h-LC50	–	–	–	–	–	>20	C	SU	Williams and Dusenbery 1990	SC
worm	*Tubifex tubifex*		24h-EC50 (immob.)	7.6	30	5.8	400	245	1080	C	SR	Khangarot 1991	SA
			48h-EC50 (Immob.)	7.6	30	5.8	400	245	920	C	SR	Khangarot 1991	SA
			96h-EC50 (immob.)	7.6	30	5.8	400	245	678	C	SR	Khangarot 1991	SC

Table 2. Aquatic Toxicity Table for Antimony

Common Name	Species Name	Life Stage	(1) Response	pH	Temp. (°C)	DO (mg/L)	Alk. (mg/L)	Hard. (mg/L)	Effact Conc. (mg/L)	(2) Chem Spec.	(3) Data Code	Reference	(4) Data Class
OTHER ORGANISMS													
algae	*Chlorella vulgaris*		NOEC (growth)	7	–	–	–	–	3.9	D**	SU	Den Dooren De Jong 1963	SC
			LOEC (growth)	7	–	–	–	–	7.8	D**	SU	Den Dooren De Jong 1963	SC
algae	*Selenastrum capricornutum*		96h–EC50 (chlor. a inhib.)	–	–	–	–	–	0.61	B	NP	USEPA 1978	SC
			96h–EC50 (cell # red.)	–	–	–	–	–	0.63	B	NP	USEPA 1978	SC
duckweed	*Lemna minor*		96h–red. growth	7.2	24	94%	47	61	25.5		SM	Brooke et al. 1986	SC

Definitions

1. Response

LC – Lethal Concentration
EC – Effect Concentration
** – units are g.atm/l
* – this study started with a nominal suspension of 100 mg Sb/l, see text for details
NOEC – No Effect Concentration
LOEC – Lowest Effect Concentration
red. – Reduction

2. Chemical Species

A – Sb as antimony potassium tartrate
B – Sb as antimony trioxide
C – Sb as antimony trichloride
D – Sb as antimony oxychloride

3. Data Codes

F – Flowthrough
S – Static
R – Renewal
M – Measured
U – Unmeasured
* – Unknown
A – Ancillary
** – 2° data because > 10% toxicant loss

4. Data Class

P – Primary
S – Secondary
A – Acute
C – Chronic

Table 3: UNCERTAINTY FACTOR WORKSHEET

CHEMICAL:	CAS No.	CONCENTRATION UNITS
Antimony	various	mg/L

Test Conditions		Species	Toxicity End Point	Effect conc.	Data Codes [1]	Data Type [2]	Calibration Factor	Reference
ACUTE	VERTEBRATE	Fathead minnow	96h-LC50	21.9	FM	1°	0.8	Kimball (undated MS)
		Rainbow trout	96h-LC50	37	SM	1°	0.8	Doe et al. 1987
		Goldfish (promoted from chronic)	7d-LC50	11.3	RM	1°	0.8	Birge 1978
	INVERT.	*Daphnia magna*	48h-LC50	5	SM	1°	0.8	Doe et al. 1987
		Gammarus psaudolimneus	96h-LC25	25.7	SM*	2°	0.9	Brooke et al. 1986
CHRONIC	VERTEBRATE	Rainbow trout	30d-LC50	16	RM	1°	0.5	Doe et al. 1987
		Fathead minnow	30d-LOEC (growth)	2.3	FM	1°	0.5	Kimball (undated MS)
		Toad *Gastrophyne carolinensis*	7d-LC50	0.3	RM	1°	0.5	Birge 1978
	INVERT.	*Hydra sp.*	96h-EC50	0.5	SM*	2°	0.7	Brooke et al. 1986
		Daphnia magna	30d-reprod.	1.7	SM	1°	0.5	Doe et al. 1987
	PLANT	*Lemna minor*	96h-red. gr.	25.5	SM	2°	0.9	Brooke et al. 1986

CALCULATION OF FINAL UNCERTAINTY FACTOR:

Since compound does not bioaccumulate, the Baseline Uncertainty Factor = 1000

Baseline Uncertainty Factor X Calibration Factors (maximum number = 11)

1000 X .8 X .8 X .8 X .8 X .9 X .5 X .5 X .5 X .7 X .5 X .9

= 14.5 FINAL UNCERTAINTY FACTOR

CRITICAL VALUE ÷ FINAL UNCERTAINTY FACTOR = Interim PWQO

= 0.3 ÷ 14.5 = 0.02 mg/L

[1] Assign 2 DATA CODES, one from each of the following rows:

S = static R = static/renewal F = flowthrough
U = unmeasured nominal conc. M = measured conc.
* = >10% loss of toxicant, therefore 2° data

[2] DATA TYPE:

1° = Primary 2° = Secondary 3° = Simulated Data
? = Unknown (Default Data Quality = 2°)

FIG. 1: DERIVATION GRAPH - ANTIMONY